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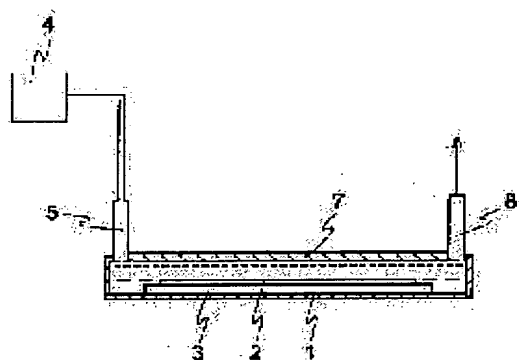
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(54) METHOD OF AND APPARATUS FOR TREATING SURFACE OF SUBSTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To increase a treating speed by using high concentration ozone efficiently by making a structure at least from an ozone supply port to an object to be treated sealable so that no gas/liquid interface exists between the ozone solution supply port and the object.

SOLUTION: A high concentration ozone aqueous solution produced by an ozone aqueous solution generator 4 is supplied from an ozone solution supply port 5 to a reaction treatment tray 1 of about 1 m² cross-sectional area and 0.05 m depth, and a silicon substrate 3 coated with a photoresist film 2 is placed in the liquid of the tray 1. A plate-shaped lid 7 is fitted to the tray 1, and the solution in the tray 1 is sealed. The supplied ozone solution is discharged from an ozone discharge opening 8. In this way, in a process in which the high concentration ozone solution is brought into contact with an object to be treated, since no gas/liquid interface exists between the supply port 5 and the object, the release of the dissolved ozone into a gas phase can be prevented, and the dissolved ozone can efficiently be used.



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CLAIMS

[Claim(s)]

[Claim 1] The substrate surface treatment approach characterized by considering as the structure which can seal said from ozone feed hopper to a processed material at least in the process which contacts a high concentration ozone solution to a processed material so that a gas-liquid interface may not exist in from an ozone solution feed hopper before a processed material.

[Claim 2] The substrate surface treatment approach characterized by making ozone exist in a gaseous phase in the process which contacts a high concentration ozone solution to a processed material.

[Claim 3] The substrate surface treatment approach according to claim 1 which installs a lid in the upper part part of a reaction processing container, and is characterized by sealing.

[Claim 4] The substrate surface treatment approach according to claim 1 characterized by contacting the dissolution ozone concerned to a processed material using an ozone solution injection nozzle with a configuration similar to the configuration of a processed material before dissolution ozone reaches a gas-liquid interface.

[Claim 5] The substrate surface treatment approach according to claim 2 which controls emission into the gaseous phase of dissolution ozone by introducing the ozone gas which occurred with the ozonator to the gaseous-phase part in a reaction processing container.

[Claim 6] The substrate surface treatment approach according to claim 2 which controls emission into the gaseous phase of dissolution ozone by introducing the ozone gas discharged from the ozone solution manufacture process to the gaseous-phase part in a reaction processing container.

[Claim 7] The substrate surface treatment approach characterized by using an acetone, an acetic acid, or its mixed solution as a solvent which dissolves ozone in the process which contacts a high concentration ozone solution to a processed material.

[Claim 8] The substrate surface treatment approach according to claim 2 characterized by the pressure of the ozone gas to supply being more than atmospheric pressure.

[Claim 9] It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The ozone solution feed hopper and ozone exhaust port which are connected with this reaction processing container, Substrate surface treatment equipment characterized by consisting of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this feed hopper, filling up with an ozone solution in said reaction processing container, and becoming so that a gas-liquid interface may not exist in from said ozone solution feed hopper before a processed material.

[Claim 10] It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The ozone solution feed hopper and ozone exhaust port which are connected with this reaction processing container, Substrate surface treatment equipment characterized by consisting of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this feed hopper, leaving a gaseous phase, supplying an ozone solution in said reaction processing container, and

coming to supply ozone into the gaseous phase in this reaction processing container.

[Claim 11] It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The sample base whose rotation of said processed material is enabled, and the ozone solution feed hopper which counters said processed material and is connected with said reaction processing container, It consists of an ozone exhaust port connected with said reaction processing container, and an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this ozone solution feed hopper. Substrate surface treatment equipment characterized by a processed material coming to be contacted before an ozone solution injection nozzle with a configuration similar to the configuration of said processed material approaches said processed material, it connects with said ozone solution feed hopper free [attachment and detachment] and the dissolution ozone from said ozone feed hopper forms a gas-liquid interface.

[Claim 12] The substrate surface-treatment equipment characterized by to consist of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container, and an ozonator of a controlling-emission into gaseous phase of dissolution ozone sake from the ozone solution feed hopper and gas-supply opening which is used for the process which contacts a high-concentration ozone solution to a processed material, and are connected with a reaction processing container and this reaction processing container and an ozone exhaust port, and this ozone solution feed hopper.

[Claim 13] It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The ozone solution feed hopper and gas supply opening which are connected with this reaction processing container, and an ozone exhaust port, It consists of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this ozone solution feed hopper. Substrate surface treatment equipment characterized by coming to introduce the ozone gas which said ozone water manufacturing installation is connected to gas supply opening by the interconnecting tube, and was discharged from said ozone water manufacturing installation from said gas supply opening to the gaseous-phase part in said reaction processing container.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the substrate surface-treatment approach and the equipment which perform improvement in the wettability on exfoliation of the photoresist film, removal of a surface particle, removal of a metal contamination, formation of an insulating oxide film, and the front face of a substrate, and adhesion using the solution which dissolved high-concentration ozone to the substrate overlying like a large-scale integrated circuit (VLSI) on the occasion of manufacture of the semi-conductor with which super-[detailed-izing and] defecation is demanded, or manufacture of the liquid-crystal substrate with which super-washing-ization is demanded.

[0002]

[Description of the Prior Art] There was the following to perform surface treatment of a substrate conventionally.

[0003] A. The exfoliation tub which exfoliates a photoresist with exfoliation liquid, and the tank rinsed with the pure water containing ozone remove a photoresist completely, and there are some which raise the yield so that it may be indicated by 1st conventional example JP,9-22867,A. Ozone water is used for the latter washing tub in order to carry out oxidation removal of the organic thin film residue which remained in the substrate slightly at the time of resist exfoliation.

[0004] As shown in drawing 10, the tank 52 made to circulate through exfoliation liquid 51 is installed in another object by the exfoliation tub 50, and the sensor 53 which measures exfoliation liquid concentration is installed in this tank 52. And at the time of a concentration fall, the new exfoliation liquid of exfoliation liquid is introduced into a tank 52 from the new liquid feeder 54 based on the signal of this sensor 53. The exfoliation liquid in a tank 52 always holds setting concentration, and the exfoliation liquid maintained at this setting concentration is supplied to said exfoliation tub 50 by supply of this new exfoliation liquid. Thereby, the substrate 55 which applied the photoresist film is made immersed at right angles to the exfoliation tub 50, and the photoresist film is removed by the exfoliation liquid injected from the injection nozzle 56 in liquid which can carry out parallel translation. Furthermore, in order to carry out oxidation removal of the organic thin film residue which remained slightly at the time of resist exfoliation, a substrate 55 is rinsed with the pure water which contains ozone in the washing tub 57.

[0005] By the conventional example 1, the solvent power over the photoresist film of a solution is made to maintain, and the amount of the exfoliation liquid used can be decreased. Moreover, the yield of photoresist film removal can be improved by washing the organic thin film which remained in the substrate front face after exfoliation with the pure water containing ozone.

[0006] B. It consists of the organic-substance removal process of removing the organic substance which adhered to the substrate by supplying the ultrapure water containing ozone to a substrate so that it may be indicated by 2nd conventional example JP,8-181137,A, a process which etches the oxide film generated at this organic substance removal process by the hydrofluoric acid, and an oxide film formation process which is contacted with the ultrapure water which contains ozone after that, and forms an oxide film, and there are some which form

the outstanding insulating oxide film in a silicon-wafer front face.

[0007] Each of said organic substance removal processes, etching processes, and oxide-film formation processes is performed one by one by the sealing tub 101 shown in drawing 11.

[0008] Where nitrogen gas is introduced from the inert gas inlet 102 of drawing 11, pure water is supplied to the rotating wafer 103 from the drug solution supply nozzle 104, it is rotated, and a wafer front face is soaked in homogeneity.

[0009] Then, ozone water is stopped and pure water washes, after forming an oxide film in this wafer front face, while supplying 2 ppm ozone addition ultrapure water from a nozzle 104 and oxidizing the organic substance on the front face of a wafer, where a wafer 103 is rotated.

[0010] Next, where a wafer 103 is rotated, a hydrofluoric-acid water solution is supplied from a nozzle 104, and the oxide film generated at the organic substance removal process is etched. After etching termination, a hydrofluoric-acid solution is stopped and pure water washes.

[0011] Next, ozone addition ultrapure water is supplied to the wafer 103 which rotated from a nozzle 104, and a 0.6nm oxide film is formed in a wafer front face. Finally, it dries by rotating a wafer 103.

[0012] Since the conventional example 2 enables it to improve the property of the oxide film of a silicon wafer sharply, high performance and a high accumulation device are realized more.

[0013]

[Problem(s) to be Solved by the Invention] There is a trouble which is listed to the next in said 1st and 2nd conventional example.

[0014] (1) In order to improve processing speed, it is possible to raise the ozone level in a water solution. However, in said conventional example, the reaction processing container is released by the gaseous phase, since the interface between an ozone solution and a gaseous phase exists, ozone will be emitted into a gaseous phase and the ozone which dissolved cannot be used effectively.

[0015] (2) Since ozone has the property to be hard to melt into water, in case it manufactures high-concentration ozone water, it needs a lot of ozone gas.

[0016] This invention was made in consideration of such a problem, and aims at offering the deployment approach of a high concentration ozone solution and equipment which can reuse the ozone gas needed for improving processing speed, using high concentration ozone effectively and ozone water manufacture.

[0017]

[Means for Solving the Problem] In the process which contacts a high concentration ozone solution to a processed material, the substrate surface treatment approach according to claim 1 is characterized by considering as the structure which can seal said from ozone feed hopper to a processed material at least so that a gas-liquid interface may not exist in from an ozone solution feed hopper before a processed material.

[0018] Moreover, the substrate surface treatment approach according to claim 2 is characterized by making ozone exist in a gaseous phase in the process which contacts a high concentration ozone solution to a processed material.

[0019] Moreover, in the process which contacts a high concentration ozone solution to a processed material, the substrate surface treatment approach according to claim 3 installs a lid in the upper part part of a reaction processing container, and is characterized by filling a reaction processing container with a solution.

[0020] Moreover, in the process which contacts a high concentration ozone solution to a processed material, using the ozone solution injection nozzle with a configuration similar to the configuration of a processed material, the substrate surface treatment approach according to claim 4 is characterized by contacting the dissolution ozone concerned to a processed material, before dissolution ozone reaches a gas-liquid interface.

[0021] Moreover, the substrate surface treatment approach according to claim 5 is characterized by controlling emission into the gaseous phase of dissolution ozone in the process which contacts a high concentration ozone solution to a processed material by introducing the ozone gas which occurred with the ozonator to the gaseous-phase part in a reaction processing container.

[0022] Moreover, the substrate surface treatment approach according to claim 6 is characterized by controlling discharge into the gaseous phase of dissolution ozone in the process which contacts a high concentration ozone solution to a processed material by introducing the ozone gas discharged from the ozone solution manufacture process to the gaseous-phase part in a reaction processing container.

[0023] Moreover, the substrate surface treatment approach according to claim 7 is characterized by using an acetone, an acetic acid, or its mixed solution as a solvent which dissolves ozone in the process which contacts a high concentration ozone solution to a processed material.

[0024] Moreover, the substrate surface treatment approach according to claim 8 is characterized by the pressure of the ozone gas which makes exist it and supplies ozone into a gaseous phase being more than atmospheric pressure in the process which contacts a high concentration ozone solution to a processed material.

[0025] Furthermore, substrate surface treatment equipment according to claim 9 It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The ozone solution feed hopper and ozone exhaust port which are connected with this reaction processing container, It is characterized by filling up with an ozone solution in said reaction processing container, and becoming so that it may consist of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this feed hopper and a gas-liquid interface may not exist in from said ozone solution feed hopper before a processed material.

[0026] Moreover, substrate surface treatment equipment according to claim 10 It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The ozone solution feed hopper and ozone exhaust port which are connected with this reaction processing container, It is characterized by consisting of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this feed hopper, leaving a gaseous phase, supplying an ozone solution in said reaction processing container, and coming to supply ozone into the gaseous phase in this reaction processing container.

[0027] Moreover, substrate surface treatment equipment according to claim 11 It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The sample base whose rotation of said processed material is enabled, and the ozone solution feed hopper which counters said processed material and is connected with said reaction processing container, It consists of an ozone exhaust port connected with said reaction processing container, and an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this ozone solution feed hopper. Before an ozone solution injection nozzle with a configuration similar to the configuration of said processed material approaches said processed material, it connects with said ozone solution feed hopper free [attachment and detachment] and the dissolution ozone from said ozone feed hopper forms a gas-liquid interface, it is characterized by a processed material coming to be contacted.

[0028] Moreover, substrate surface treatment equipment according to claim 12 It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The ozone solution feed hopper and gas supply opening which are connected with this reaction processing container, and an ozone exhaust port, It is characterized by consisting of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container, and an ozonator of a controlling-emission into gaseous phase of dissolution ozone sake from this ozone solution feed hopper.

[0029] Moreover, substrate surface treatment equipment according to claim 13 It is used for the process which contacts a high concentration ozone solution to a processed material. A reaction processing container, The ozone solution feed hopper and gas supply opening which are connected with this reaction processing container, and an ozone exhaust port, It consists of an ozone water manufacturing installation which supplies an ozone solution to said reaction processing container from this ozone solution feed hopper. Said ozone water manufacturing

installation is connected to gas supply opening by the interconnecting tube, and it is characterized by coming to introduce the ozone gas discharged from said ozone water manufacturing installation from said gas supply opening to the gaseous-phase part in said reaction processing container.

[0030]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail.

[0031] The schematic diagram of the experimental device with which gestalt 1 drawing 1 of operation explains the gestalt 1 of operation of this invention, and drawing 2 are the schematic diagrams of the substrate surface treatment equipment in which the gestalt 1 of operation of this invention is shown.

[0032] With the gestalt of this operation, a high concentration ozone solution is supplied in a reaction processing container, and the ozone level in a solution is measured. In drawing 1, the ozone solution feed hopper for leading the ozone water with which the reaction processing tray whose 1a is a reaction processing container, and 4 were manufactured by the ozone water manufacturing installation, and 5 was manufactured by this ozone water manufacturing installation 4 to reaction processing tray 1a, and 6 are overflow **. In drawing 2, since it has the structure where reaction processing tray 1b can seal a solution, the ozone water generated by the ozone water manufacturing installation 4 is supplied without a gas-liquid interface from the ozone solution feed hopper 5. In addition, 8 is an ozone exhaust port. The art shown in claim 1 by abolishing a gas-liquid interface is enforced. The effectiveness of an art shown in claim 1 by comparing by the case where there are not a case where there is a gas-liquid interface, and a gas-liquid interface is shown.

[0033] The ozone level in the solution generated by drawing 3 by the ozone manufacturing installation, the ozone level in the case of drawing 1, and the ozone level in the case of drawing 2 are shown.

[0034] As shown in drawing 3, when there is an interface between a high concentration ozone solution and a gaseous phase and ozone does not exist in a gaseous phase, the ozone which dissolved is partially emitted into a gaseous phase, and the ozone level fall in a solution is seen. On the other hand, it turns out that a reaction processing container is filled up with a high concentration ozone solution, a concentration fall is not seen but the ozone which dissolved can be used effectively since the ozone in a solution is not emitted into a gaseous phase when a gas-liquid interface does not exist in before the processed material immersed from an ozone solution feed hopper.

[0035] Where gestalt 2 processed material of operation is *(ed) in a reaction processing container, the high concentration ozone solution was supplied in the reaction processing container, and the ozone level in the solution near the processing substrate was measured. The art shown in claim 2 according to making ozone exist in a gaseous phase is enforced. The effectiveness of an art according to claim 2 is shown by comparing the case where ozone does not exist in the case where ozone gas exists in a gaseous phase, and a gaseous phase.

[0036] The result of having measured the ozone level about the case where ozone does not exist in the case where ozone exists in drawing 4 in a gaseous phase, and a gaseous phase is shown.

[0037] When there was an interface between a high concentration ozone solution and a gaseous phase and ozone did not exist in a gaseous phase, the ozone which dissolved was partially emitted into the gaseous phase, and the ozone level fall in a solution was seen. On the other hand, since the ozone of a solution is hard to be emitted into a gaseous phase when ozone is supplied into the gaseous phase in this reaction processing container and ozone exists in the gaseous phase in this reaction processing container, while a high concentration ozone solution is supplied in a reaction processing container, a concentration fall is controlled and the ozone which dissolved can be used effectively.

[0038] Gestalt 3 drawing 5 and drawing 6 of operation are the schematic diagram of the experimental device in which the gestalt 3 of operation of this invention is shown. All are aimed at exfoliation of the photoresist film 2 applied on the silicon substrate 3 which is a processed

material.

[0039] In drawing 5, the high concentration ozone water generated by the ozone water manufacturing installation 4 from the ozone solution feed hopper 5 on the reaction processing tray 1 (2 cross-section a depth of 0.05m of 1m) is supplied, and the silicon substrate 3 which applied the photoresist film 2 into the liquid of the reaction processing tray 1 is installed. The supplied ozone water is discharged from overflow ** 6.

[0040] In drawing 6, the high concentration ozone water generated by the ozone water manufacturing installation 4 from the ozone solution feed hopper 5 on the reaction processing tray 1 (2 cross-section a depth of 0.05m of 1m) is supplied, and the silicon substrate 3 which applied the photoresist film 2 into the liquid of the reaction processing tray 1 is installed. The plate-like lid 7 was installed in the reaction processing tray 1, and the solution in the reaction processing tray 1 is sealed. The supplied ozone water is discharged from the ozone exhaust port 8.

[0041] The surface treatment approach of claim 3 is enforced by using the substrate surface treatment equipment of a configuration of that drawing 6 showed. Moreover, the effectiveness by invention according to claim 3 becomes clear by comparing the result of the equipment of drawing 5.

[0042] As a processing substrate, what applied the 6-micrometer resist to the 8 inches silicon wafer was used. 200 mL/min and ozone water concentration changed the ozone water flow rate with 10, 20, and 50 ppm.

[0043] The exfoliation rate of a resist was computed by measuring the film thickness.

[0044] A result is shown in Table 1. The effectiveness of being about 1.5 to 2 twice many as this was seen as an exfoliation rate by installing a lid.

[0045]

[Table 1]

表 1

	蓋 有／無	オゾン水濃度 (ppm)	剥離速度 ($\mu\text{m}/\text{min}$)
比較例 1	無	10	0.046
比較例 2	無	20	0.075
比較例 3	無	50	0.15
実施例 1	有	10	0.061
実施例 2	有	20	0.13
実施例 3	有	50	0.289

[0046] In the gestalt 3 of gestalt 4 implementation of operation, by using an acetone, an acetic acid, or its mixed solution in addition to water showed that there was effectiveness of high resist exfoliation as a solvent which dissolves ozone. This is that the solubility of the ozone to an acetone and an acetic acid is higher than water, and is considered to be because for the ozone level in a solution to have increased.

[0047] A resist exfoliation rate improves by the solubility to an ozone solution being small instead of the lid 7 in the gestalt 3 of gestalt 5 implementation of operation, for example, covering a solution side with oil films, such as a silicone oil, to it. When it covered with the 1-2mm oil film and the same experiment as the gestalt 3 of operation was conducted, as compared with the case where there is no oil film, the effectiveness of being twice [1.4 to] many as this was seen.

[0048] Gestalt 6 drawing 7 of operation is the schematic diagram showing the gestalt 6 of operation of this invention. It aims at formation of a pure oxide film on the silicon substrate.

[0049] In drawing 7, the ozone water generated by the ozone water manufacturing installation 14 is introduced into the reaction-vessel body 10 which is a reaction processing container from

a feed hopper 15. The 8 inch silicon substrate 12 is installed on the sample base 13 with the device to rotate. The gas after the waste fluid exhaust port 16 and a reaction is discharged for the solution after a reaction from an exhaust port 17. Gas can be supplied if needed from the gas supply opening 18.

[0050] A silicon substrate 12 is installed on the sample base 13, introducing nitrogen gas from the gas supply opening 18. Three cc of ultrapure water was supplied from the feed hopper 20, the sample base 13 was rotated by 500rpm, and the front face was wet.

[0051] By substrate rotational frequency 3000rpm, high concentration ozone water (20 ppm) was supplied for 1 minute by 300 cc/min from the feed hopper 15, and clarification was carried out with pure water after removing the organic contamination on a front face.

[0052] Then, by substrate rotational frequency 3000rpm, the hydrofluoric-acid water solution was supplied for 2 minutes by 30 cc/min 0.5% from the feed hopper 21, and pure water washed after etching a surface oxide film.

[0053] The ozone solution injection nozzle 19 which has the structure of the configuration of a substrate 12 and a similar configuration in a feed hopper 15 next is connected, and by substrate rotational frequency 3000rpm, supply 20 ppm ozone water for 30 seconds by 400 cc/min from this nozzle 19, before dissolution ozone reaches a gas-liquid interface, a processed material is made to contact, and an oxide skin is formed in a substrate front face. Spacing of said nozzle 19 and substrate 12 is 0.5-1.0mm.

[0054] The substrate surface treatment approach according to claim 4 is enforced by using the substrate surface treatment equipment of a configuration of that drawing 7 showed. Moreover, the effectiveness of this invention becomes clear by the comparison with the case where the ozone solution injection nozzle 19 is removed.

[0055] The result of having measured the oxide skin 30 seconds after ozone water treatment is shown in Table 2. The thickness of an oxide film increased 1.3 to 1.5 times by the ozone solution injection nozzle 19.

[0056] A reactant low acetone, an acetic acid, or its mixed solution with ozone etc. can be used like the gestalt 4 of operation as a solvent which dissolves ozone in addition to water.

[0057]

[Table 2]

表 2

	ノズル 有/無	酸化膜の厚さ (nm)
比較例 4	無	1.0
実施例 4	有	1.48
実施例 5	有	1.33
実施例 6	有	1.3

[0058] The gestalt 7 of gestalt 7 implementation of operation aims at formation of a pure oxide film on the silicon substrate.

[0059] In drawing 8, 30 introduces a reaction-vessel body and the ozone water generated by the ozone water manufacturing installation 34 from a feed hopper 35. The 8 inch silicon substrate 32 is installed on the sample base 33 with the device to rotate. The gas after the waste fluid exhaust port 36 and a reaction is discharged for the solution after a reaction from an exhaust port 37. Gas can be supplied if needed from the gas supply opening 38.

[0060] A silicon substrate 32 is installed on the sample base 33, introducing nitrogen gas from the gas supply opening 38. Three cc of ultrapure water was supplied from the feed hopper 40, the sample base 33 was rotated by 500rpm, and the front face was wet.

[0061] By substrate rotational frequency 3000rpm, high concentration ozone water (20 ppm) was supplied for 1 minute by 300 cc/min from the feed hopper 35, and pure water washed after removing the organic contamination on a front face.

[0062] Then, by substrate rotational frequency 3000rpm, the hydrofluoric-acid water solution

was supplied for 2 minutes by 300 cc/min 0.5% from the feed hopper 41, and pure water washed after etching a surface oxide film.

[0063] Next, by substrate rotational frequency 3000rpm, supplying the ozone gas of 50-300g/Nm³ generated with the ozonator 42 from the gas supply opening 38, 20 ppm ozone water is supplied for 30 seconds by 400 cc/min from a feed hopper 35, and an oxide skin is formed in a substrate front face.

[0064] The substrate surface treatment approach according to claim 5 is enforced by using the substrate surface treatment equipment of a configuration of that drawing 8 showed. Moreover, the effectiveness of this invention becomes clear by the comparison with the case where nitrogen gas is supplied from the gas supply opening 38 instead of ozone gas.

[0065] The result of having measured the oxide skin 30 seconds after ozone water treatment is shown in Table 3. The thickness of an oxide film increased 1.4 to 1.6 times by ozone gas supply.

[0066] An acetone, an acetic acid, or its mixed solution can be used like the gestalt 4 of operation as a solvent which dissolves ozone in addition to water.

[0067]

[Table 3]

表 3

	供給ガス	酸化膜の厚さ (nm)
比較例 5	窒素	1.0
実施例 7	オゾン	1.63
実施例 8	オゾン	1.53
実施例 9	オゾン	1.43

[0068] In the gestalt 7 of gestalt 8 implementation of operation, even when the ozone gas of the high-pressure force is supplied instead of supplying the high concentration ozone gas of ordinary pressure from the gas supply opening 38, the thickness of an oxide skin increases. As compared with the case where nitrogen gas is supplied, the thickness of an oxide film increased 1.3 to 1.6 times by supplying 3 from the gas supply opening 38 the pressure of two or more atmospheric pressures, and the ozone gas concentration of 20-30g/Nm. The more the supply-gas-pressure force is high, the more it is effective, but if the safety of equipment is taken into consideration, it can be said that two to 5 atmospheric pressure is suitable.

[0069] In the gestalt 7 of gestalt 9 implementation of operation, as ozone gas supplied from the gas supply opening 38, as shown in drawing 9, the gas supply opening 38 is connected with the ozone water manufacturing installation 34 by the interconnecting tube 43, and the substrate surface treatment approach according to claim 6 is enforced by using the ozone gas discharged from the ozone water manufacturing installation 34.

[0070] 20 ppm ozone water is supplied for 30 seconds by 400 cc/min from a feed hopper 35, and in order to control emission into the gaseous phase of dissolution ozone in parallel to the processing which forms an oxide skin in a substrate front face, the ozone gas of three or more [50g //Nm] discharged from the ozone water manufacturing installation 34 is supplied to the gaseous-phase part in the reaction processing container 30 from the ozone feed hopper 38 through an interconnecting tube 43. The oxide skin which had one 1.2 to 1.6 times the thickness of this from the gas supply opening 38 as compared with the case where nitrogen is supplied has been formed.

[0071]

[Effect of the Invention] Since a gas-liquid interface will be abolished in the process which contacts a high concentration ozone solution to a processed material according to invention according to claim 1 by the time a high concentration ozone solution contacts a processed material from a feed hopper as explained above While being able to use effectively the ozone which could prevent emission into the gaseous phase of the ozone which dissolved, and dissolved in the process using a high concentration ozone solution Since a high concentration

ozone solution has the powerful oxidation, it performs photoresist exfoliation and an oxide-film formation process quickly, and can process them efficiently.

[0072] Moreover, since ozone is made to exist in a gaseous phase in the process which contacts a high concentration ozone solution to a processed material according to invention according to claim 2, emission into the gaseous phase of the ozone which dissolved can be prevented, and the ozone which dissolved in the process using a high concentration ozone solution can be used effectively.

[0073] Moreover, since according to invention according to claim 3 the lid was installed in the upper part part of a reaction processing container and it sealed into it in the process which contacts a high concentration ozone solution to a processed material, emission into the gaseous phase of the ozone which dissolved by filling a reaction processing container with a solution can be prevented, and the ozone which dissolved in the process using a high concentration ozone solution can be used effectively.

[0074] Moreover, since a processed material is made to contact using an ozone solution injection nozzle with a configuration similar to the configuration of a processed material according to invention according to claim 4 before dissolution ozone reaches a gas-liquid interface, emission into the gaseous phase of the ozone which dissolved can be prevented, and the ozone which dissolved in the process using a high concentration ozone solution can be used effectively.

[0075] Moreover, since emission into the gaseous phase of dissolution ozone is controlled by introducing the ozone gas which occurred with the ozonator to the gaseous-phase part in a reaction processing container according to invention according to claim 5, emission into the gaseous phase of the ozone which dissolved can be prevented, and the ozone which dissolved in the process using a high concentration ozone solution can be used effectively.

[0076] Moreover, since emission into the gaseous phase of dissolution ozone is controlled by introducing the ozone gas discharged from the ozone solution manufacture process to the gaseous-phase part in a reaction processing container according to invention according to claim 6, emission into the gaseous phase of the ozone which dissolved can be prevented, and the ozone which dissolved in the process using a high concentration ozone solution can be used effectively. Moreover, by this, the ozone gas discharged not only from a deployment of a high concentration ozone solution but from ozone solution manufacture can be used effectively.

[0077] Moreover, according to invention according to claim 7, a high concentration ozone solution is set in the process contacted to a processed material. When the solubility to ozone uses a certain acetone, an acetic acid, or its mixed solution about 10 times as a solvent which dissolves ozone as compared with water Especially, in the washing process of the organic substance etc., the cleaning effect by the ozone solution can be remarkably raised by the rather than thing for which an oleophilic high acetone is used, using water with oleophilic [low] as a solvent.

[0078] Moreover, since the pressure of the ozone gas by which ozone exists and supplies a high concentration ozone solution into a gaseous phase in the process contacted to a processed material is more than atmospheric pressure according to invention according to claim 8, while being able to control emission into the gaseous phase of the ozone which dissolved by introducing high-pressure ozone gas, the film thickness of an oxide skin can be made to increase.

[0079] Since emission into the gaseous phase of the ozone which dissolved can furthermore be prevented according to invention according to claim 9 to 13, the ozone which dissolved in the process using a high concentration ozone solution can be used effectively.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram of the experimental device explaining the gestalt 1 of operation of this invention.

[Drawing 2] It is the schematic diagram of the substrate surface treatment equipment in which the gestalt 1 of operation of this invention is shown.

[Drawing 3] It is drawing showing the ozone level in the solution generated by the ozone manufacturing installation, the ozone level in the case of drawing 1 , and the ozone level in the case of drawing 2 .

[Drawing 4] It is drawing showing the result of having measured the ozone level about the case where ozone does not exist in the case where ozone exists in a gaseous phase, and a gaseous phase.

[Drawing 5] It is the schematic diagram of the experimental device explaining the gestalten 3, 4, and 5 of operation of this invention.

[Drawing 6] It is the schematic diagram of the substrate surface treatment equipment in which the gestalten 3, 4, and 5 of operation of this invention are shown.

[Drawing 7] It is the schematic diagram of the substrate surface treatment equipment in which the gestalt 6 of operation of this invention is shown.

[Drawing 8] It is the schematic diagram of the substrate surface treatment equipment in which the gestalten 7 and 8 of operation of this invention are shown.

[Drawing 9] It is the schematic diagram of the substrate surface treatment equipment in which the gestalt 9 of operation of this invention is shown.

[Drawing 10] It is the schematic diagram of the equipment in which the conventional example 1 is shown.

[Drawing 11] It is the schematic diagram of the equipment in which the conventional example 2 is shown.

[Description of Notations]

1 Reaction Processing Tray, 2 Photoresist Film, 3 Silicon Substrate, 4 An ozone water manufacturing installation, 5 An ozone solution feed hopper, 6 Overflow **, 7 A lid, 8 An ozone exhaust port, 10 A reaction-vessel body, 12 Silicon substrate, 13 A sample base, 14 An ozone water manufacturing installation, 15 Ozone solution feed hopper, 16 A solution exhaust port, 17 Gas exhaust, 18 Gas supply opening, 19 Ozone solution injection nozzle, 20 A pure-water feed hopper, 21 hydrofluoric-acid feed hopper, 30 Reaction-vessel body, 32 A silicon substrate, 33 A sample base, 34 Ozone water manufacturing installation, 35 An ozone solution feed hopper, 36 Solution exhaust port 37 gas exhaust, 38 Gas supply opening, 40 A pure-water feed hopper, 41 Hydrofluoric-acid feed hopper, 42 An ozonator, 43 An interconnecting tube, 50 An exfoliation tub, 51 Exfoliation liquid, 52 tanks, 53 A sensor, 54 A new liquid feeder, 55 A substrate, 56 The injection nozzle in liquid, 57 A washing tub, 101 A sealing tub, 102 An inert gas inlet, 103 Wafer 104 Drug solution supply nozzle.

[Translation done.]

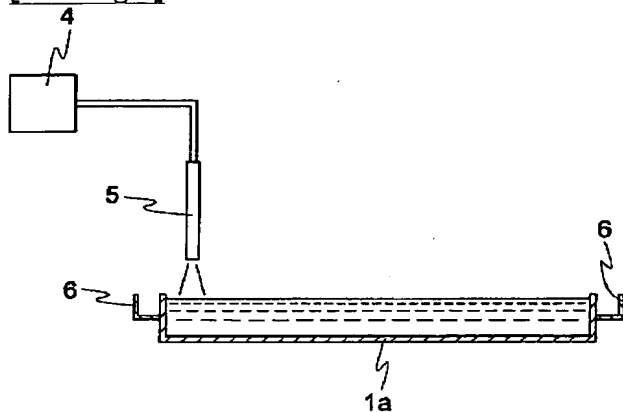
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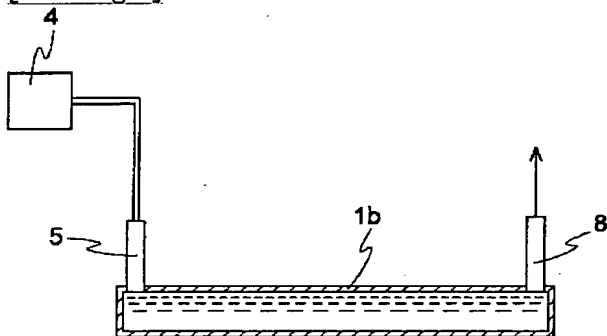
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DRAWINGS

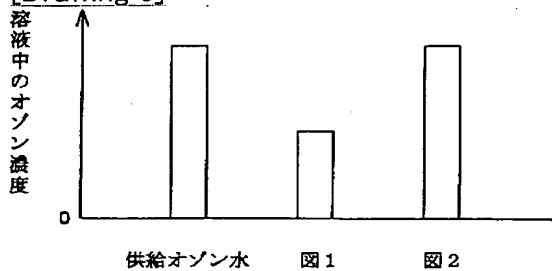
[Drawing 1]



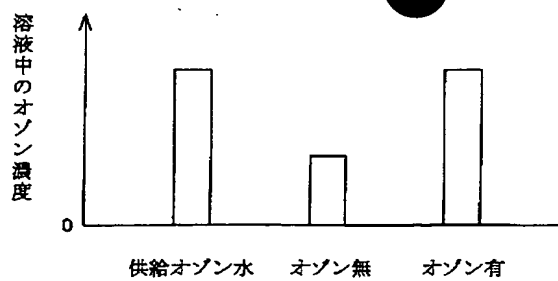
[Drawing 2]



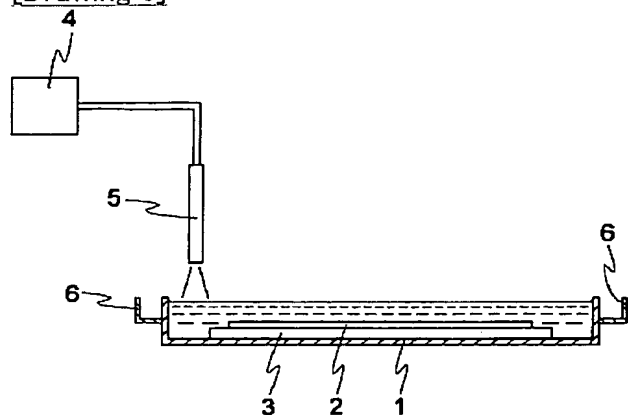
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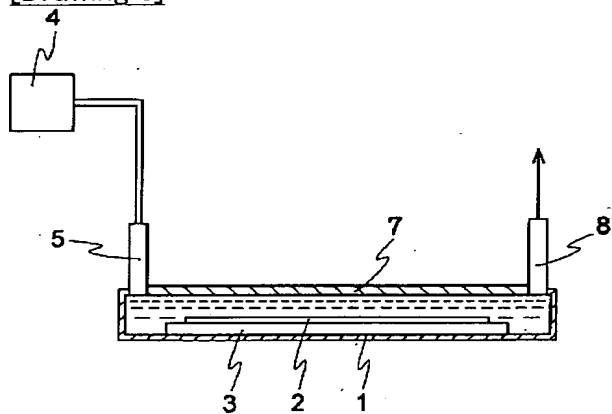
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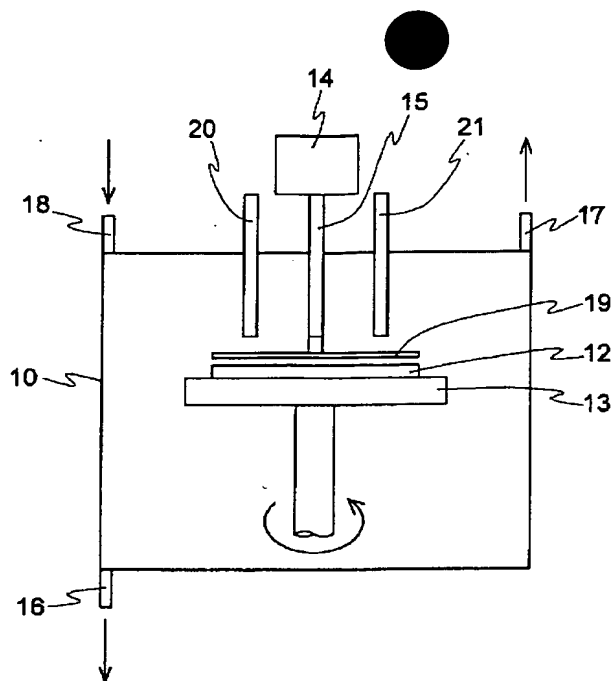
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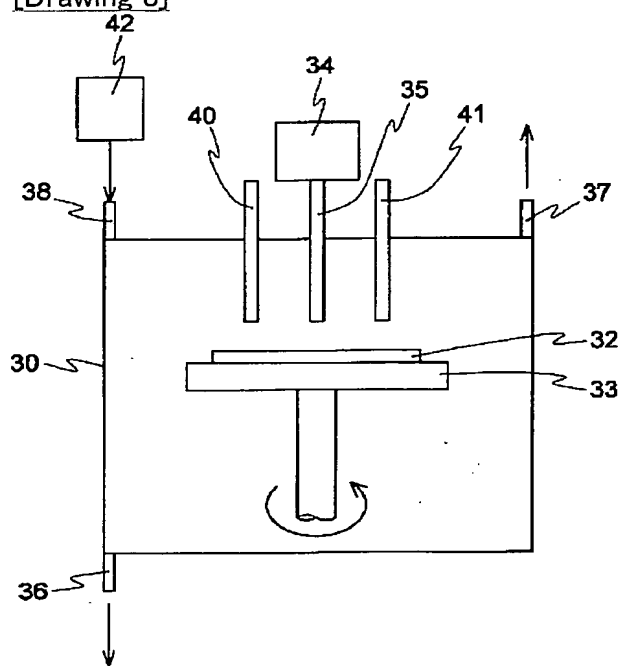
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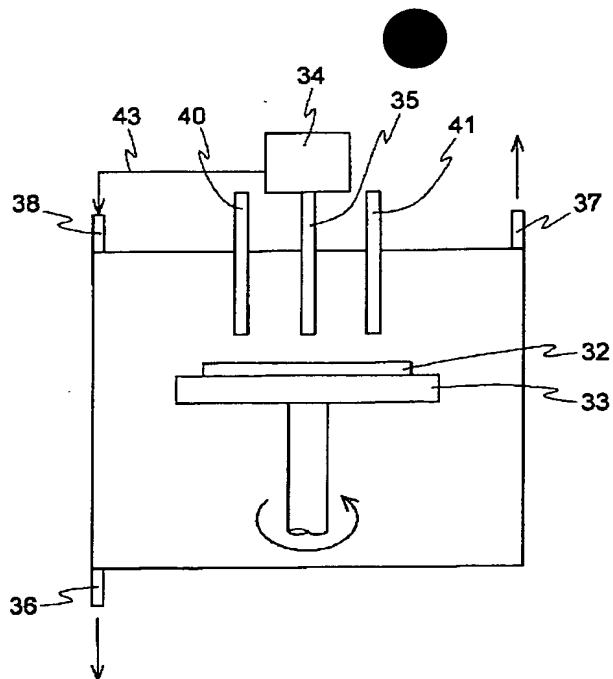
[Drawing 7]



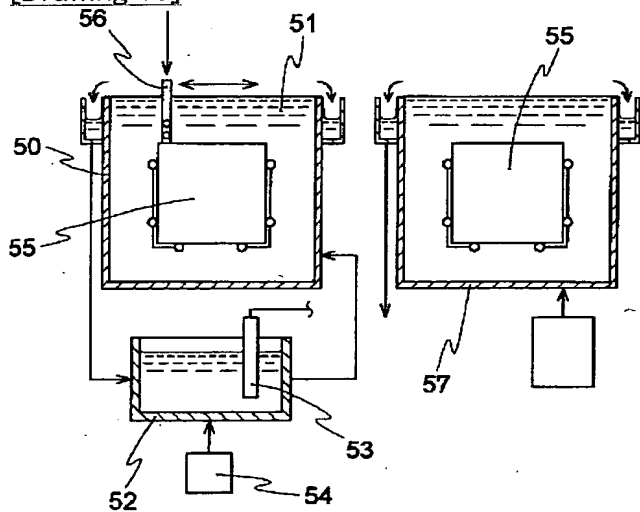
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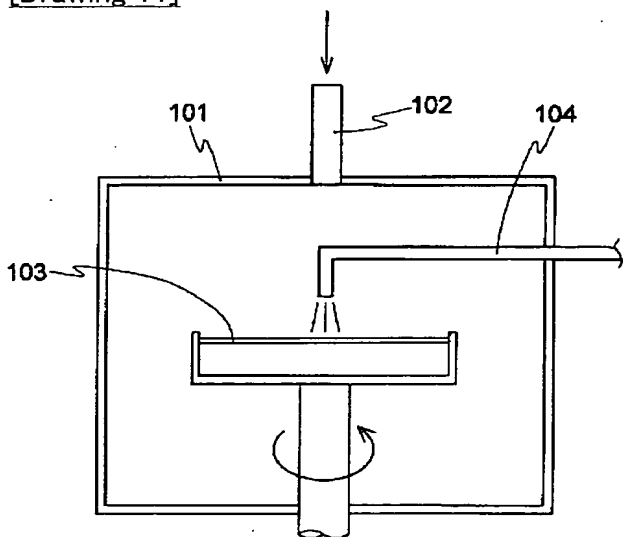
[Drawing 9]



[Drawing 10]



[Drawing 11]



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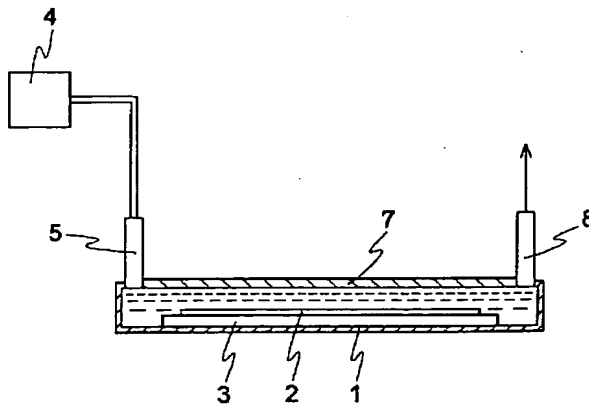
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(54) 【発明の名称】 基板表面処理方法および装置

(57) 【要約】

【課題】 高濃度オゾン溶液を利用するプロセスにおいて、高濃度オゾン溶液を有効利用し、処理速度向上のための基板表面処理方法を提供する。

【解決手段】 高濃度オゾン溶液を被処理物である基板3に接触させるプロセスにおいて、オゾン溶液供給口5から被処理物である基板3までの間に気液界面が存在しないように少なくとも前記オゾン供給口5から基板3までを密閉し得る構造とした。



【特許請求の範囲】

【請求項 1】 高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、オゾン溶液供給口から被処理物までの間に気液界面が存在しないように少なくとも前記オゾン供給口から被処理物までを密閉し得る構造としたことを特徴とする基板表面処理方法。

【請求項 2】 高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、気相中にオゾンが存在させることを特徴とする基板表面処理方法。

【請求項 3】 反応処理容器の上方部分に蓋を設置し、密閉することを特徴とする請求項 1 記載の基板表面処理方法。

【請求項 4】 被処理物の形状に類似した形状をもつオゾン溶液噴射ノズルを用いて、溶解オゾンが気液界面に達する前に当該溶解オゾンを被処理物に接触させることを特徴とする請求項 1 記載の基板表面処理方法。

【請求項 5】 オゾン発生器によって発生したオゾンガスを反応処理容器内の気相部分へ導入することによって、溶解オゾンの気相中への放出を抑制する請求項 2 記載の基板表面処理方法。

【請求項 6】 オゾン溶液製造プロセスから排出されたオゾンガスを反応処理容器内の気相部分へ導入することによって、溶解オゾンの気相中への放出を抑制する請求項 2 記載の基板表面処理方法。

【請求項 7】 高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、オゾン溶解する溶媒としてアセトン、酢酸またはその混合溶液を用いることを特徴とする基板表面処理方法。

【請求項 8】 供給するオゾンガスの圧力が大気圧以上であることを特徴とする請求項 2 記載の基板表面処理方法。

【請求項 9】 高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結されるオゾン溶液供給口およびオゾン排出口と、該供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記オゾン溶液供給口から被処理物までの間に気液界面が存在しないように、前記反応処理容器内にオゾン溶液が充填されてなることを特徴とする基板表面処理装置。

【請求項 10】 高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結されるオゾン溶液供給口およびオゾン排出口と、該供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記反応処理容器内に気相を残してオゾン溶液を供給し、該反応処理容器内の気相中にオゾンが供給されてなることを特徴とする基板表面処理装置。

【請求項 11】 高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、前記被処理物を回転自在にする試料台と、前記被処理物に対向して

前記反応処理容器に連結されるオゾン溶液供給口と、前記反応処理容器に連結されるオゾン排出口と、該オゾン溶液供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記被処理物の形状に類似した形状をもつオゾン溶液噴射ノズルが前記被処理物に近接して前記オゾン溶液供給口に着脱自在に接続され、前記オゾン供給口からの溶解オゾンが気液界面を形成する前に被処理物に接触されてなることを特徴とする基板表面処理装置。

【請求項 12】 高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結されるオゾン溶液供給口、ガス供給口およびオゾン排出口と、該オゾン溶液供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置と、溶解オゾンの気相中への放出を抑制するためのオゾン発生器とからなることを特徴とする基板表面処理装置。

【請求項 13】 高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結されるオゾン溶液供給口、ガス供給口およびオゾン排出口と、該オゾン溶液供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記オゾン水製造装置がガス供給口に連結管により接続されており、前記オゾン水製造装置から排出されたオゾンガスが前記ガス供給口から前記反応処理容器内の気相部分へ導入されてなることを特徴とする基板表面処理装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、超大型規模集積回路（超 LSI）のように、微細化、超清浄化が要求される半導体の製造、または超洗浄化が要求される液晶基板の製造に際し、基板に対して高濃度オゾンを溶解した溶液を利用して、フォトリソ膜の剥離、表面微粒子の除去、金属汚染物の除去、絶縁酸化膜の形成、基板表面の濡れ性および密着性の向上を行う基板表面処理方法および装置に関するものである。

【0002】

【従来の技術】基板の表面処理を行うものとしては、従来、以下のようなものがあった。

【0003】A. 第 1 従来例

特開平 9-22867 号公報に開示されるように、剥離液にてフォトリソを剥離する剥離槽と、オゾンを含む純水にて水洗する水槽によって、フォトリソを完全に除去し、歩留まりを向上させるものがある。レジスト剥離時にわずかに基板に残った有機薄膜残渣を酸化除去するために、後段の洗浄槽にはオゾン水が用いられている。

【0004】図 10 に示すように、剥離槽 50 には、剥離液 51 を循環させるタンク 52 が別体に設置され、該タンク 52 内に剥離液濃度を測定するセンサー 53 が設

置されている。そして濃度低下時には、該センサー53の信号に基づいて新液供給装置54から剥離液の新しい剥離液がタンク52に導入される。この新しい剥離液の供給により、タンク52内の剥離液は常時設定濃度を保持し、この設定濃度に保たれた剥離液は前記剥離槽50に供給される。これにより、フォトレジスト膜を塗布した基板55を剥離槽50に垂直に浸漬させ、平行移動できる液中噴射ノズル56から噴射された剥離液によってフォトレジスト膜は除去される。さらに、レジスト剥離時にわずかに残った有機薄膜残渣を酸化除去するために、洗浄槽57においてオゾンを含む純水にて基板55を水洗する。

【0005】従来例1によって、溶解液のフォトレジスト膜に対する溶解力を持続させ、剥離液の使用量を減少できる。また、剥離後の基板表面に残った有機薄膜をオゾンを含む純水で洗浄することでフォトレジスト膜除去の歩留まりを向上できる。

【0006】B. 第2従来例

特開平8-181137号公報に開示されるように、オゾンを含む超純水を基板に供給することにより基板に付着した有機物を除去する有機物除去工程と、該有機物除去工程で生成する酸化膜をフッ化水素酸によってエッチングする過程と、その後にオゾンを含む超純水と接触されて酸化膜を形成する酸化膜形成工程とからなり、シリコンウエハ表面に絶縁性の優れた酸化膜を形成するものがある。

【0007】前記有機物除去工程、エッチング工程および酸化膜形成工程は何れも図11に示す密閉槽101で順次行われる。

【0008】図11の不活性ガス導入口102から窒素ガスを導入した状態で、回転するウエハ103に薬液供給ノズル104から純水を供給して、回転させウエハ表面を均一に濡らす。

【0009】続いて、ウエハ103を回転した状態で、2ppmのオゾン添加超純水をノズル104より供給してウエハ表面の有機物を酸化させるとともに、該ウエハ表面に酸化膜を形成した後、オゾン水を止めて純水で洗浄する。

【0010】つぎに、ウエハ103を回転した状態で、ノズル104からフッ化水素酸水溶液を供給して、有機物除去工程で生成した酸化膜をエッチングする。エッチング終了後、フッ化水素酸溶液を止めて純水で洗浄する。

【0011】つぎに、回転したウエハ103にノズル104からオゾン添加超純水を供給して、ウエハ表面に0.6nmの酸化膜を形成する。最後に、ウエハ103を回転させることで乾燥する。

【0012】従来例2によって、たとえばシリコンウエハの酸化膜の特性を大幅に改善することが可能になるため、より高性能、高集積デバイスが実現される。

【0013】

【発明が解決しようとする課題】前記第1および第2従来例では、つぎに挙げるような問題点がある。

【0014】(1)処理速度を向上するために、水溶液中のオゾン濃度を高めることが考えられる。しかしながら、前記従来例においては、反応処理容器が気相に解放されており、オゾン溶液と気相間の界面が存在するためにオゾンが気相中に放出されてしまい、溶解したオゾンを有効利用できない。

10 【0015】(2)オゾンは水に溶けにくい性質をもつため、高濃度のオゾン水を製造する際には多量のオゾンガスを必要とする。

【0016】本発明は、このような問題を考慮してなされたもので、高濃度オゾンを有効に利用して処理速度を向上すること、かつ、オゾン水製造のために必要とされたオゾンガスを再利用することができる高濃度オゾン溶液の有効利用方法および装置を提供することを目的とする。

【0017】

20 【課題を解決するための手段】請求項1記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、オゾン溶液供給口から被処理物までの間に気液界面が存在しないように、少なくとも前記オゾン供給口から被処理物までを密閉し得る構造としたことを特徴としている。

【0018】また、請求項2記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、気相中にオゾンを存在させることを特徴としている。

30 【0019】また、請求項3記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、反応処理容器の上方部分に蓋を設置し、反応処理容器を溶液で満たすことを特徴としている。

【0020】また、請求項4記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、被処理物の形状に類似した形状をもつオゾン溶液噴射ノズルを用いて、溶解オゾンが気液界面に達する前に当該溶解オゾンを被処理物に接触させることを特徴としている。

40 【0021】また、請求項5記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、オゾン発生器によって発生したオゾンガスを反応処理容器内の気相部分へ導入することによって、溶解オゾンの気相中への放出を抑制することを特徴としている。

50 【0022】また、請求項6記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、オゾン溶液製造プロセスから排出されたオゾンガスを反応処理容器内の気相部分へ導入することによって、溶解オゾンの気相中への排出を抑制することを特

徴としている。

【0023】また、請求項7記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、オゾンを溶解する溶媒としてアセトン、酢酸またはその混合溶液を用いることを特徴としている。

【0024】また、請求項8記載の基板表面処理方法は、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、気相中にオゾンを存在させ、かつ、供給するオゾンガスの圧力が大気圧以上であることを特徴としている。

【0025】さらに、請求項9記載の基板表面処理装置は、高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結されるオゾン溶液供給口およびオゾン排出口と、該供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記オゾン溶液供給口から被処理物までの間に気液界面が存在しないように、前記反応処理容器内にオゾン溶液が充填されてなることを特徴としている。

【0026】また、請求項10記載の基板表面処理装置は、高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結されるオゾン溶液供給口およびオゾン排出口と、該供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記反応処理容器内に気相を残してオゾン溶液を供給し、該反応処理容器内の気相中にオゾンが供給されてなることを特徴としている。

【0027】また、請求項11記載の基板表面処理装置は、高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、前記被処理物を回転自在にする試料台と、前記被処理物に対向して前記反応処理容器に連結されるオゾン溶液供給口と、前記反応処理容器に連結されるオゾン排出口と、該オゾン溶液供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記被処理物の形状に類似した形状をもつオゾン溶液噴射ノズルが前記被処理物に近接して前記オゾン溶液供給口に着脱自在に接続され、前記オゾン供給口からの溶解オゾンが気液界面を形成する前に被処理物に接触されてなることを特徴としている。

【0028】また、請求項12記載の基板表面処理装置は、高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結されるオゾン溶液供給口、ガス供給口およびオゾン排出口と、該オゾン溶液供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置と、溶解オゾンの気相中への放出を抑制するためのオゾン発生器とからなることを特徴としている。

【0029】また、請求項13記載の基板表面処理装置は、高濃度オゾン溶液を被処理物に接触させるプロセスに用いられ、反応処理容器と、該反応処理容器に連結さ

れるオゾン溶液供給口、ガス供給口およびオゾン排出口と、該オゾン溶液供給口から前記反応処理容器にオゾン溶液を供給するオゾン水製造装置とからなり、前記オゾン水製造装置がガス供給口に連結管により接続されており、前記オゾン水製造装置から排出されたオゾンガスが前記ガス供給口から前記反応処理容器内の気相部分へ導入されてなることを特徴としている。

【0030】

【発明の実施の形態】以下、本発明の実施の形態を詳細に説明する。

【0031】実施の形態1

図1は本発明の実施の形態1を説明する実験装置の概略図、図2は本発明の実施の形態1を示す基板表面処理装置の概略図である。

【0032】本実施の形態では、反応処理容器内に高濃度オゾン溶液を供給し、溶液中のオゾン濃度を測定する。図1において、1aは反応処理容器である反応処理トレー、4はオゾン水製造装置、5は該オゾン水製造装置4で製造されたオゾン水を反応処理トレー1aに導くためのオゾン溶液供給口、6はオーバーフロー樋である。図2においては、反応処理トレー1bが溶液を密閉できる構造になっているので、オゾン水製造装置4で生成されたオゾン水がオゾン溶液供給口5から気液界面なく供給される。なお、8はオゾン排出口である。気液界面をなくすことで請求項1に示される処理方法が実施される。気液界面のある場合と気液界面のない場合で比較することで請求項1に示した処理方法の有効性が示される。

【0033】図3にオゾン製造装置によって生成される溶液中のオゾン濃度、図1の場合のオゾン濃度および図2の場合のオゾン濃度を示す。

【0034】図3に示すように、高濃度オゾン溶液と気相間の界面があり、かつ、気相中にオゾンが存在しない場合には、溶解したオゾンは部分的に気相中へ放出され、溶液中のオゾン濃度低下が見られる。これに対し、反応処理容器に高濃度オゾン溶液が充填され、オゾン溶液供給口から、浸漬される被処理物までの間に気液界面が存在しない場合には、溶液中のオゾンが気相中へ放出されないため、濃度低下が見られず、溶解したオゾンを有効利用できることがわかる。

【0035】実施の形態2

被処理物を反応処理容器中に漬した状態で、反応処理容器内に高濃度オゾン溶液を供給し、処理基板近傍での溶液中のオゾン濃度を測定した。気相中にオゾンを存在させることで請求項2に示した処理方法が実施される。気相中にオゾンガスが存在する場合と気相中にオゾンが存在しない場合を比較することで請求項2記載の処理方法の有効性が示される。

【0036】図4に気相中にオゾンが存在する場合と気相中にオゾンが存在しない場合についてオゾン濃度を測

定した結果を示す。

【0037】高濃度オゾン溶液と気相間の界面があり、かつ、気相中にオゾンが存在しない場合には、溶解したオゾンは部分的に気相中へ放出され、溶液中のオゾン濃度低下が見られた。これに対し、反応処理容器内に高濃度オゾン溶液が供給されるとともに、該反応処理容器内の気相中にオゾンを供給し、該反応処理容器内の気相中にオゾンが存在する場合には、溶液のオゾンが気相中へ放出されにくいので、濃度低下が抑制され、溶解したオゾンを有効利用できる。

【0038】実施の形態3

図5および図6は本発明の実施の形態3を示す実験装置の概略図である。いずれも被処理物であるシリコン基板3上に塗布したフォトリソ膜2の剥離を目的としている。

【0039】図5において、反応処理トレー1（断面積1m²、深さ0.05m）にオゾン溶液供給口5からオゾン水製造装置4で生成した高濃度オゾン水を供給し、反応処理トレー1の液中にフォトリソ膜2を塗布したシリコン基板3を設置する。供給されたオゾン水はオーバーフロー樋6から排出される。

【0040】図6において、反応処理トレー1（断面積

表 1

	蓋 有／無	オゾン水濃度 (ppm)	剥離速度 (μm/min)
比較例1	無	10	0.046
比較例2	無	20	0.075
比較例3	無	50	0.15
実施例1	有	10	0.061
実施例2	有	20	0.13
実施例3	有	50	0.289

【0046】実施の形態4

実施の形態3において、オゾンを溶解する溶媒として水以外に、アセトン、酢酸またはその混合溶液などを使用することにより、高いレジスト剥離の効果があることがわかった。これは、水よりもアセトン、酢酸へのオゾンの溶解度が高いことで、溶液中のオゾン濃度が増大したことによるものと考えられる。

【0047】実施の形態5

実施の形態3における蓋7の代わりに、オゾン溶液に対する溶解度が小さい、たとえばシリコンオイルなどの油膜で溶液面を覆うことによって、レジスト剥離速度は改善される。1～2mmの油膜で覆って実施の形態3と同様の実験を行ったところ、油膜がない場合と比較して1.4～2倍の効果が見られた。

【0048】実施の形態6

図7は本発明の実施の形態6を示す概略図である。シリ

1m²、深さ0.05m）にオゾン溶液供給口5からオゾン水製造装置4で生成した高濃度オゾン水を供給し、反応処理トレー1の液中にフォトリソ膜2を塗布したシリコン基板3を設置する。反応処理トレー1には平板状の蓋7が設置され、反応処理トレー1内の溶液を密封している。供給されたオゾン水はオゾン排出口8から排出される。

【0041】図6で示した構成の基板表面処理装置を用いることで請求項3の表面処理方法が実施される。また、図5の装置の結果を比較することで請求項3記載の発明による効果が明確になる。

【0042】処理基板として、8インチのシリコンウエハに6μmのレジストを塗布したものをを用いた。オゾン水流量は200mL/min、オゾン水濃度は10、20および50ppmと変化させた。

【0043】レジストの剥離速度は、その膜厚さを測定することで算出した。

【0044】結果を表1に示す。蓋を設置することで剥離速度として約1.5～2倍の効果が見られた。

【0045】

【表1】

コン基板上に清浄な酸化膜の形成を目的としている。

【0049】図7において、反応処理容器である反応槽本体10にオゾン水製造装置14によって生成したオゾン水を供給口15から導入する。回転する機構をもった試料台13上に、8インチシリコン基板12を設置する。反応後の溶液は廃液排出口16および反応後のガスは排出口17から排出される。ガス供給口18から必要に応じてガスを供給できる。

【0050】ガス供給口18から窒素ガスを導入しながら、シリコン基板12を試料台13上に設置する。供給口20から超純水を3cc供給し、500rpmで試料台13を回転して表面を濡らした。

【0051】基板回転数3000rpmで、供給口15から高濃度オゾン水（20ppm）を300cc/minで1分間供給して、表面上の有機汚染物を除去後、純水で清浄した。

【0052】続いて基板回転数3000rpmで、供給口21から0.5%フッ化水素酸水溶液を30cc/minで2分間供給して表面の酸化膜をエッチング後、純水で洗浄した。

【0053】つぎに、供給口15に基板12の形状と類似した形状の構造をもつオゾン溶液噴射ノズル19を接続し、基板回転数3000rpmで、該ノズル19から20ppmのオゾン水を400cc/minで30秒間供給して、溶解オゾンが気液界面に達する前に被処理物に接触させ、基板表面に酸化被膜を形成する。前記ノズル19と基板12の間隔は0.5~1.0mmである。

【0054】図7で示した構成の基板表面処理装置を用

表 2

	ノズル 有/無	酸化膜の厚さ (nm)
比較例 4	無	1.0
実施例 4	有	1.48
実施例 5	有	1.33
実施例 6	有	1.3

【0058】実施の形態7

実施の形態7はシリコン基板上に清浄な酸化膜の形成を目的としている。

【0059】図8において、30は反応槽本体、オゾン水製造装置34によって生成したオゾン水を供給口35から導入する。回転する機構をもった試料台33上に、8インチシリコン基板32を設置する。反応後の溶液は廃液排出口36および反応後のガスは排出口37から排出される。ガス供給口38から必要に応じてガスを供給

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【0060】ガス供給口38から窒素ガスを導入しながら、シリコン基板32を試料台33上に設置する。供給口40から超純水を3cc供給し、500rpmで試料台33を回転して表面を濡らした。

【0061】基板回転数3000rpmで、供給口35から高濃度オゾン水(20ppm)を300cc/minで1分間供給して、表面上の有機汚染物を除去後、純水で洗浄した。

【0062】続いて基板回転数3000rpmで、供給口41から0.5%フッ化水素酸水溶液を300cc/minで2分間供給して表面の酸化膜をエッチング後、

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いることで請求項4記載の基板表面処理方法が実施される。また、オゾン溶液噴射ノズル19を取り外した場合との比較によって、本発明の効果が明らかになる。

【0055】オゾン水処理30秒後の酸化被膜を測定した結果を表2に示す。オゾン溶液噴射ノズル19によって酸化膜の厚さは1.3~1.5倍になった。

【0056】実施の形態4と同様に、オゾンを溶解する溶媒として水以外に、オゾンとの反応性の低いアセトン、酢酸またはその混合溶液などを使用することができ

【0057】

【表2】

純水で洗浄した。

【0063】つぎに、基板回転数3000rpmで、オゾン発生器42によって生成した50~300g/Nm³のオゾンガスをガス供給口38から供給しながら、供給口35から20ppmのオゾン水を400cc/minで30秒間供給して、基板表面に酸化被膜を形成する。

【0064】図8で示した構成の基板表面処理装置を用いることで請求項5記載の基板表面処理方法が実施される。また、オゾンガスの代わりに窒素ガスをガス供給口38から供給した場合との比較によって、本発明の効果が明らかになる。

【0065】オゾン水処理30秒後の酸化被膜を測定した結果を表3に示す。オゾンガス供給によって酸化膜の厚さは1.4~1.6倍になった。

【0066】実施の形態4と同様に、オゾンを溶解する溶媒として水以外に、アセトン、酢酸またはその混合溶液などを使用することができる。

【0067】

【表3】

表 3

	供給ガス	酸化膜の厚さ (nm)
比較例 5	窒素	1.0
実施例 7	オゾン	1.63
実施例 8	オゾン	1.53
実施例 9	オゾン	1.43

【0068】実施の形態8

実施の形態7において、ガス供給口38から常圧の高濃度オゾンガスを供給する代わりに、高圧力のオゾンガスを供給した場合でも、酸化被膜の膜厚が増加する。圧力2気圧以上、オゾンガス濃度20～30g/Nm³をガス供給口38から供給することで、窒素ガスを供給した場合と比較して、酸化膜の厚さは1.3～1.6倍になった。供給ガス圧力は高めれば高いほど効果はあるが、装置の安全性を考慮すると、2～5気圧が適しているといえる。

【0069】実施の形態9

実施の形態7において、ガス供給口38から供給するオゾンガスとして、図9に示すように、オゾン水製造装置34とガス供給口38を連結管43で接続し、オゾン水製造装置34から排出されるオゾンガスを用いることで請求項6記載の基板表面処理方法が実施される。

【0070】供給口35から20ppmのオゾン水を400cc/minで30秒間供給して、基板表面に酸化被膜を形成する処理に並行して、溶解オゾンの気相中への放出を抑制するために、オゾン水製造装置34から排出された50g/Nm³以上のオゾンガスを連結管43を通してオゾン供給口38から反応処理容器30内の気相部分へ供給する。ガス供給口38から窒素を供給した場合と比較して、1.2～1.6倍の厚さをもった酸化被膜を形成できた。

【0071】

【発明の効果】以上説明した通り、請求項1記載の発明によれば、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、高濃度オゾン溶液が供給口から被処理物に接触するまでの間に気液界面をなくすので、溶解したオゾンの気相中への放出を防止することができ、高濃度オゾン溶液を用いたプロセスにおいて溶解したオゾンを有効利用できるとともに、高濃度オゾン溶液は強力な酸化作用があるため、フォトリソスト剥離や酸化膜形成プロセスを迅速に行い、効率よく処理できる。

【0072】また、請求項2記載の発明によれば、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、気相中にオゾンを存在させるので、溶解したオゾンの気相中への放出を防止することができ、高濃度オゾン溶液を用いたプロセスにおいて溶解したオゾンを有効利用できる。

【0073】また、請求項3記載の発明によれば、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、反応処理容器の上方部分に蓋を設置し、密閉したので、反応処理容器を溶液で満たすことで溶解したオゾンの気相中への放出を防止することができ、高濃度オゾン溶液を用いたプロセスにおいて溶解したオゾンを有効利用できる。

【0074】また、請求項4記載の発明によれば、被処理物の形状に類似した形状をもつオゾン溶液噴射ノズルを用いて、溶解オゾンが気液界面に達する前に被処理物に接触させるので、溶解したオゾンの気相中への放出を防止することができ、高濃度オゾン溶液を用いたプロセスにおいて溶解したオゾンを有効利用できる。

【0075】また、請求項5記載の発明によれば、オゾン発生器によって発生したオゾンガスを反応処理容器内の気相部分へ導入することによって、溶解オゾンの気相中への放出を抑制するので、溶解したオゾンの気相中への放出を防止することができ、高濃度オゾン溶液を用いたプロセスにおいて溶解したオゾンを有効利用できる。

【0076】また、請求項6記載の発明によれば、オゾン溶液製造プロセスから排出されたオゾンガスを反応処理容器内の気相部分へ導入することによって、溶解オゾンの気相中への放出を抑制するので、溶解したオゾンの気相中への放出を防止することができ、高濃度オゾン溶液を用いたプロセスにおいて溶解したオゾンを有効利用できる。またこれによって、高濃度オゾン溶液の有効利用だけでなく、オゾン溶液製造から排出されるオゾンガスを有効利用できる。

【0077】また、請求項7記載の発明によれば、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、オゾンに対する溶解度が水と比較して10倍程度あるアセトン、酢酸またはその混合溶液をオゾンを溶解する溶媒として用いていることにより、特に、有機物の洗浄プロセスなどにおいては、親油性が低い水を溶媒として用いるよりも、親油性の高いアセトンを用いることで、オゾン溶液による洗浄効果を著しく向上させることができる。

【0078】また、請求項8記載の発明によれば、高濃度オゾン溶液を被処理物に接触させるプロセスにおいて、気相中にオゾンが存在し、かつ、供給するオゾンガスの圧力が大気圧以上であるので、高圧のオゾンガスを

導入することで溶解したオゾンの気相中への放出が抑制できるとともに、酸化被膜の膜厚さを増加させることができる。

【0079】さらに請求項9～13記載の発明によれば、溶解したオゾンの気相中への放出を防止することができるので、高濃度オゾン溶液を用いたプロセスにおいて溶解したオゾンを有効利用できる。

【図面の簡単な説明】

【図1】 本発明の実施の形態1を説明する実験装置の概略図である。

【図2】 本発明の実施の形態1を示す基板表面処理装置の概略図である。

【図3】 オゾン製造装置によって生成される溶液中のオゾン濃度、図1の場合のオゾン濃度および図2の場合のオゾン濃度を示す図である。

【図4】 気相中にオゾンが存在する場合と気相中にオゾンが存在しない場合についてオゾン濃度を測定した結果を示す図である。

【図5】 本発明の実施の形態3、4、5を説明する実験装置の概略図である。

【図6】 本発明の実施の形態3、4、5を示す基板表面処理装置の概略図である。

【図7】 本発明の実施の形態6を示す基板表面処理装置の概略図である。

【図8】 本発明の実施の形態7、8を示す基板表面処理装置の概略図である。

【図9】 本発明の実施の形態9を示す基板表面処理装置の概略図である。

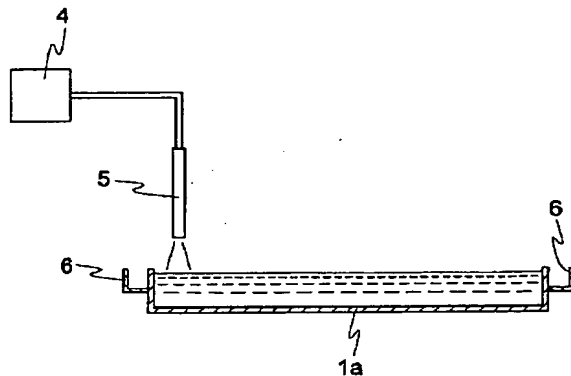
【図10】 従来例1を示す装置の概略図である。

【図11】 従来例2を示す装置の概略図である。

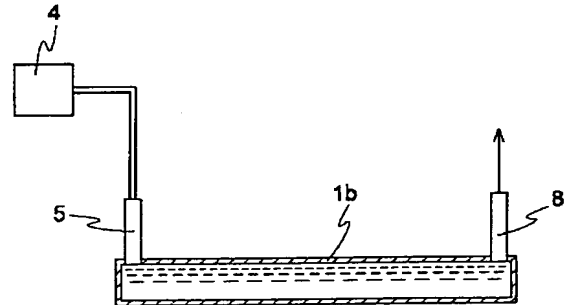
【符号の説明】

1 反応処理トレー、2 フォトリソ膜、3 シリコン基板、4 オゾン水製造装置、5 オゾン溶液供給口、6 オーバーフロー樋、7 蓋、8 オゾン排出口、10 反応槽本体、12 シリコン基板、13 試料台、14 オゾン水製造装置、15 オゾン溶液供給口、16 溶液排出口、17 ガス排出口、18 ガス供給口、19 オゾン溶液噴射ノズル、20 純水供給口、21 フッ化水素酸供給口、30 反応槽本体、32 シリコン基板、33 試料台、34 オゾン水製造装置、35 オゾン溶液供給口、36 溶液排出口、37 ガス排出口、38 ガス供給口、40 純水供給口、41 フッ化水素酸供給口、42 オゾン発生器、43 連結管、50 剥離槽、51 剥離液、52 タンク、53 センサー、54 新液供給装置、55 基板、56 液中噴射ノズル、57 洗浄槽、101 密閉槽、102 不活性ガス導入口、103 ウエハ 104 薬液供給ノズル。

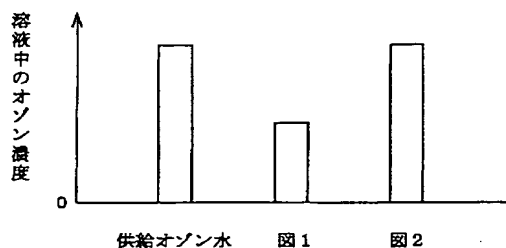
【図1】



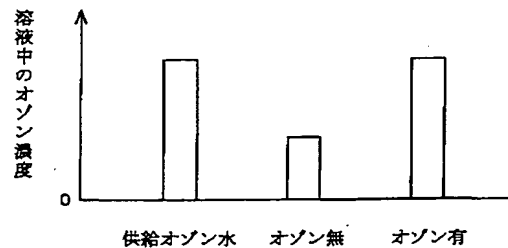
【図2】



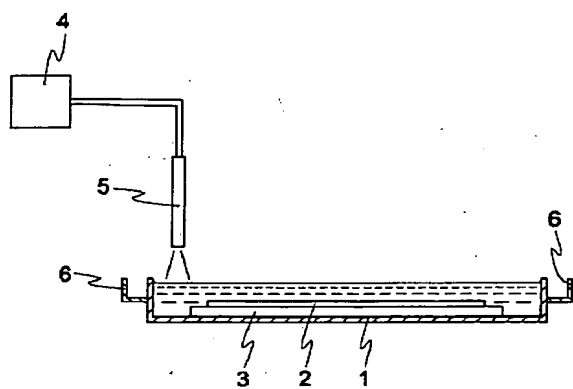
【図3】



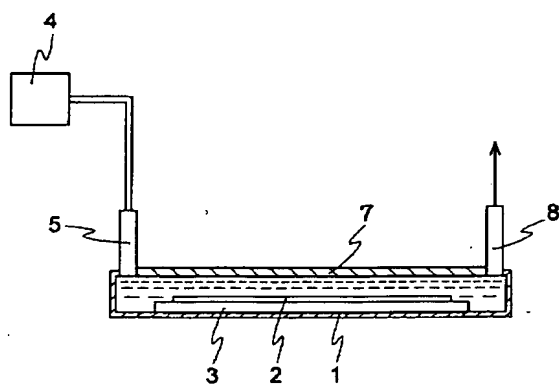
【図4】



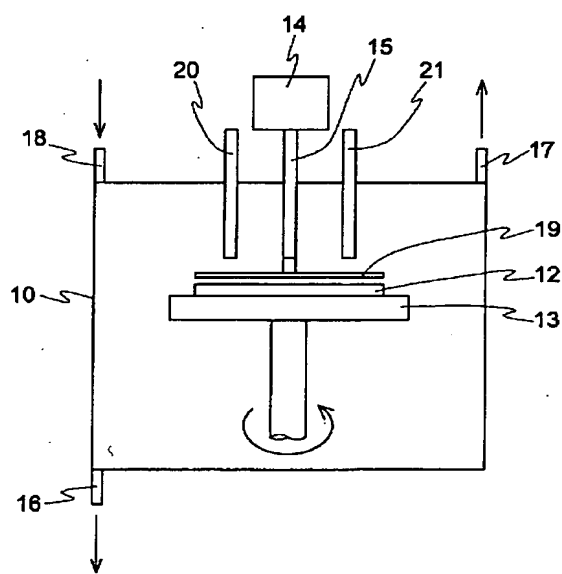
【図5】



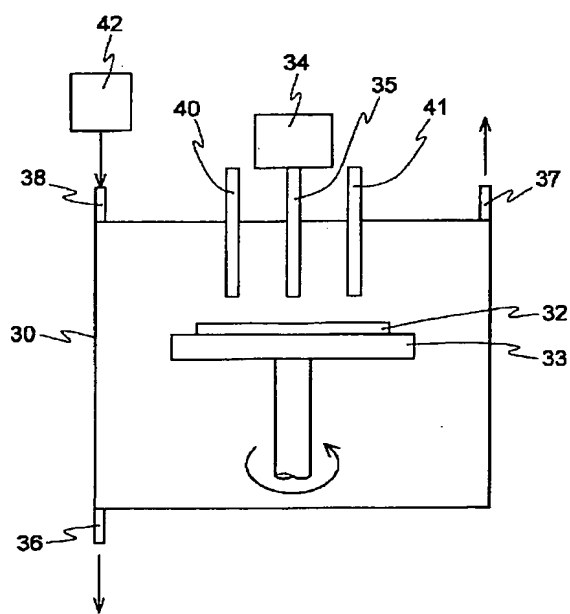
【図6】



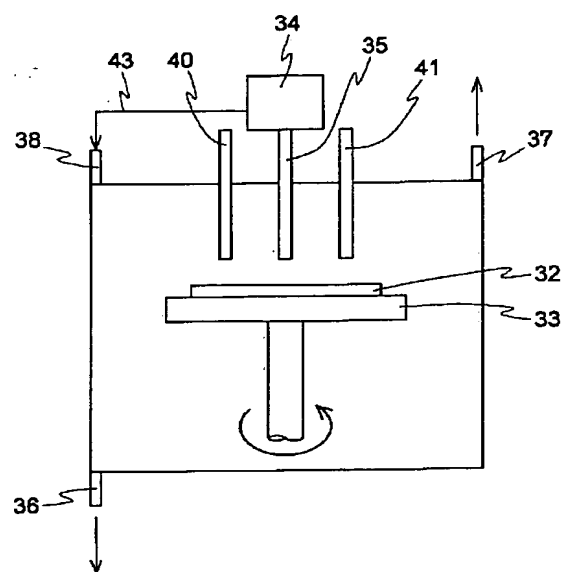
【図7】



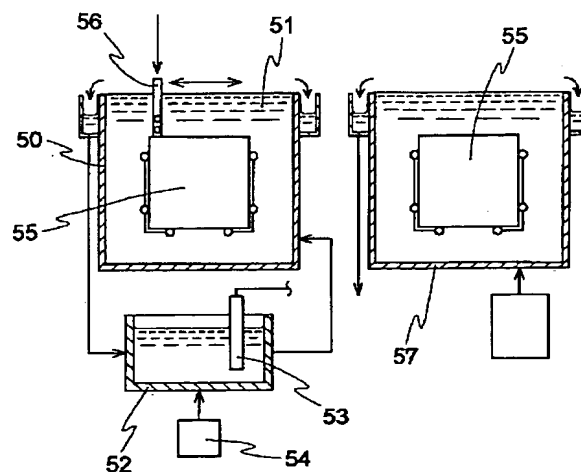
【図8】



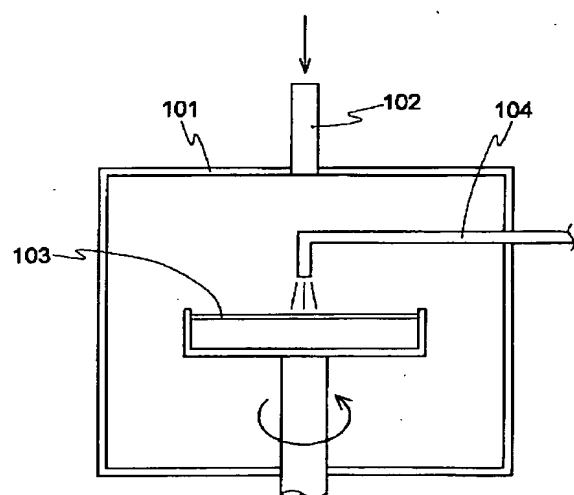
【図9】



【図10】



【図11】



フロントページの続き

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